CHEMISTRY LETTERS, pp. 1877-1880, 1990.

A New Preparative Method of Buta-1,3-diene and Hexa-1,5-dien-3-yne by Reduction of Butatriene and Hexapentaene, Respectively, with Zn-$ZnCl_2$-H_2O

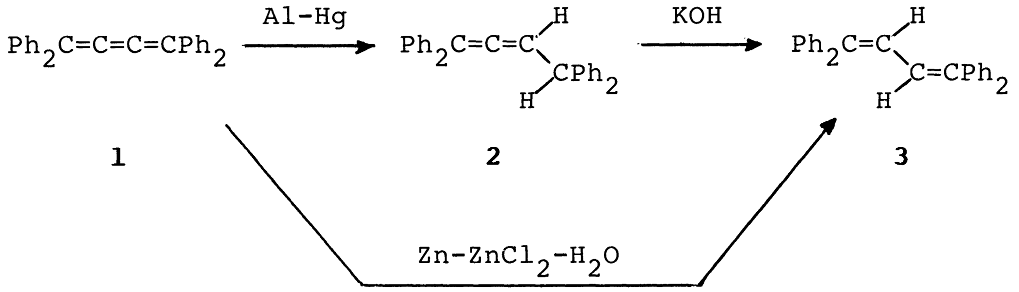
Satoshi KISHIGAMI, Koichi TANAKA, and Fumio TODA*
Department of Industrial Chemistry, Faculty of Engineering,
Ehime University, Matsuyama 790

The Zn-$ZnCl_2$-H_2O reagent was found to be effective for the reduction of aryl group substituted butatrienes and hexapentaenes to buta-1,3-dienes and hexa-1,5-dien-3-ynes, respectively.

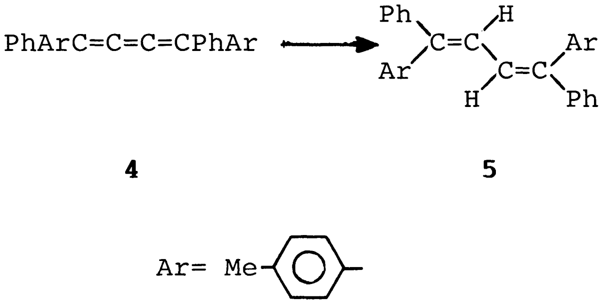
Some hexa-1,5-dien-3-yne derivatives show biological activities,1) and some synthetic routes of these have been developed.2,3) Although the synthetic method of the hexa-1,5-dien-3-yne system by a selective reduction of hexapentaene seems to be attractive because the hexapentaene is easily derived from hexa-2,4-dyne-1,6-diol, no such the selective reduction method has yet been developed so far. Only one stepwise synthetic method of 1,1,6,6-tetraarylhexa-1,5-dien-3-yne (**8**) from 1,1,6,6-tetraarylhexapentaene (**6**) via 1,1,6,6-tetraarylhexa-1,2,4,5-tetraene (**7**) has been reported (Eq. 2).4)

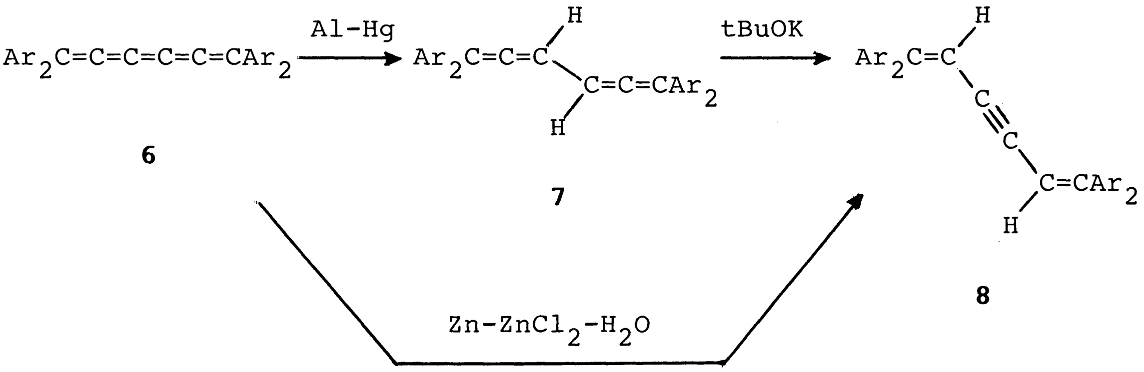
During the course of the study of new reagent Zn-salt-H_2O for the reduction of activated olefins5) and ketones,6) for the coupling of aromatic aldehydes and ketones to produce α-pinacols,7) and for the solid state Reformatsky and Luche reactions,8) we found that the reagent is very effective for the direct reduction of **1** and **6** to **3** and **8**, respectivley.

A mixture of **1** (1 g), Zn (5 g), $ZnCl_2$ (2 g), and THF-H_2O (10:1, 33 ml) was heated under reflux for 6 h, and the reaction mixture was diluted with



(1)





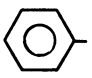
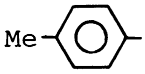
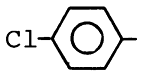
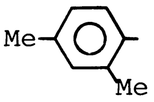
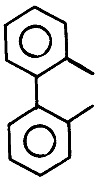
(2)

3 mol dm^{-3} HCl and extracted with toluene. Evaporation of toluene gave **3** (0.95 g, 95% yield, mp 198-201 °C (lit.[4]) mp 200 °C)). The preparative method is much simpler and more effective than the reported one which obtains **3** in 70% yield by heating at 60 °C for 2 h of a solution of **2** in KOH-MeOH initially prepared in 70% yield by Al-Hg reduction of **1** (Eq. 1).[4] By the same method, **5** (mp 223-226 °C) was derived from *trans*-**4** in 90% yield. Of three possible geometrical isomers, only one isomer was produced selectively, to which the structure of **5** is assigned tentatively.

A mixture of 1,1,6,6-tetraphenylhexapentaene **(6a)** (1 g), Zn (5 g), $ZnCl_2$ (2 g), and THF-H_2O (10:1, 33 ml) was stirred at room temperature for 10 min, and the reaction mixture was diluted with 3 mol dm^{-3} HCl and extracted with toluene. Evaporation of toluene gave 1,1,6,6-tetraphenylhexa-1,5-dien-3-yne **(8a)** (0.95 g, 95% yield, mp 170-173 °C (lit.4) mp 160 °C9))). Kuhn and Fischer have also reported that the heating for 16 h of a solution of 1,1,6,6-tetraphenylhexa-1,2,4,5-tetraene **(7a)** in tBuOK-tBuOH which had been prepared in 75% yield by Al-Hg reduction of **6a**, gives **8a** in 80% yield.4) In this case, however, our preparative method is again much simpler and more effective than the reported one.

By the same method, **8b-e** were obtained from **6b-e** in the yields shown in Table 1.

Table 1. Reaction time of the reduction of **6a-e** with Zn-$ZnCl_2$-H_2O, and yield and melting point of the product **8a-e**a)

		Product		
Ar	Reaction time / min		yield / %	mp / °
	10	**8a**	95	179-182
	10	**8b**	96	159-163
	20	**8c**	80	247-249
	10	**8d**	100	150-151
Ar_2= 	15	**8e**	90	300

a)All the reactions were carried out by stirring a mixture of **6** (1 g), Zn (5 g), $ZnCl_2$ (2 g), and THF-H_2O (10:1, 33 ml) at room temperature.

In the reduction with Al-Hg, 1,2-addition of hydrogens occurred both in **1** and **6**. However, in the reduction with Zn-$ZnCl_2$-H_2O, 1,2- and 1,4-additions of hydrogens occurred in **1** and **6**, respectively. Furthermore, Al-Hg and Zn-$ZnCl_2$-H_2O reduce the 1,2- and 2,3-positions of **1**, respectively, and the 3,4- and 2,5-positions of **6**, respectively. The preliminary formation of **2** and **7** in the reduction with Zn-$ZnCl_2$-H_2O of **1** and **6**, respectively, would be ruled out, because the rearrangement of **2** and **7** to **3** and **8**, respectively, occurs only under basic conditions.4) The difference of the reduction mode between the two reagents is interesting but the reason is not clear.

We wish to thank the Ministry of Education, Science and Culture, Japan, for Grant-in-Aid for Scientific Research on Priority Areas, No. 02210104.

References

1) E. R. H. Jones and V. Thaller, "The Chemistry of Carbon-Carbon Triple Bond, ed by S. Patai, Interscience, New York (1978), Part II, p. 621.
2) D. A. Ben-Efraim, "The Chemistry of Carbon-Carbon Triple Bond, ed by S. Patai, Interscience, New York (1978), Part II, p. 755.
3) Y. Hatanaka, K. Matsui, and T. Hiyama, Tetrahedron Lett., **30**, 2403(1989).
4) R. Kuhn and F. Fischer, Chem. Ber., **94**, 3060 (1961).
5) F. Toda and K. Iida, Chem. Lett., **1976**, 695.
6) F. Toda, K. Tanaka, and H. Tange, J. Chem. Soc., Perkin Trans. 1, **1989**, 1555.
7) K. Tanaka, S. Kishigami, and F. Toda, J. Org. Chem., **55**, 2981 (1990).
8) K. Tanaka, S. Kishigami, and F. Toda, J. Org. Chem., submitted.
9) Melting point of the **8a** prepared by our method is higher than that reported in the literature.4) The structure of the **8a** was elucidated by an X-ray crystal structural analysis. The data will be published in the near future.

(Received August 3, 1990)